

EFFECTS OF MAGNETIC FIELD ON CALCIUM CARBONATE PRECIPITATION IN STATIC AND DYNAMIC FLUID SYSTEMS

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ABSTRACT:

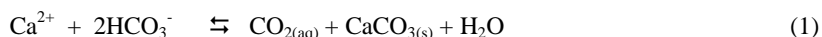
Magnetic field effect on CaCO₃ precipitation is the key parameter in evaluating the effectiveness of Magnetic Water Treatment (MWT). The purpose of this study was to investigate magnetic fields influence on CaCO₃ precipitation in static and dynamic (circulation flow) fluid system using carbonized aqueous solutions. The observation results in static fluid system showed the decrease of precipitated CaCO₃ in magnetized solutions compared to those in non-magnetic solution with their pH of 6.4 – 8. On the other hand, in dynamic fluid system, it was found that magnetic treatment increased CaCO₃ precipitation, depending on pH solution, flow rate and circulation time. The results suggest that the effects of magnetic on static and dynamic systems may occur in different phenomena. In Static fluid system, magnetic field strengthens hydrate structure in magnetized ions, which reduce precipitation process. However, in dynamic fluid system, Lorentz force and magneto-hydrodynamic effect on charged ions or particles played important role in increasing CaCO₃ precipitation.

Keywords: Magnetic field, calcium carbonate precipitation; static fluid, dynamic fluid

1. INTRODUCTION

Scale formation on pipe walls and heat exchange equipment is a serious problem encountered in almost all water processes. Typical scale deposits are composed of minerals that become less soluble with increasing temperature. Calcium carbonate is the most common deposit. Scale deposits usually form hard-to-remove-linings, which reduce water flow capacities. When they build up on the heat exchanger surfaces, heat transfer efficiency is reduced because of their low thermal conductivity.

Scale formation in hard water as CaCO₃ precipitation process is an equilibrium and slowing process. Increase of pH due to CO₂ release in solution will push precipitation of CaCO₃ as follow :



Anti-scale water treatment using chemical methods changes the solution chemistry and can be very expensive. The chemical methods for water conditioning are economically and ecologically visible especially under conditions of high circulation flow rates for large plants such as thermal power plants. In some other areas, such as food and beverage industries or residential areas, there are strict requirements for water quality.

Magnetic water treatment (MWT) is a method, where supplied or circulated water is simply exposed to a magnetic field. This method has a long and controversial history but is reported to have been effective in numerous instances. Its main effect is to either reduce scale deposit or remove existing scale or produce a softer and less tenacious scale [1]. The mechanism is still unclear, although MWT has been practically used for over half a century. According to the review paper of Baker and Judd [2], the efficiency of this treatment is still a controversial question and clear explanation of the phenomenon does not exist yet. In the same time, conclusions drawn on the basis of laboratory works sometimes are opposite to each other [3], [2]. Understanding how the magnetic field of relatively low densities precisely modifies the precipitation of low magnetic minerals such as CaCO₃ is still being developed.

Two mechanisms have been developed to address magnetic field effects on calcium carbonate precipitation in static fluid system, viz., (1) a direct effect on dissolved ions and (2) a magnetic effect on particles [4]. They called the first mechanism as “*ionic mechanism*”. Examples of ionic response to a magnetic field have been reported by Higashitani [5] who investigated the characteristics of calcium carbonate precipitation and it was found that the nucleation of calcium carbonate was suppressed. Higashitani [6]

hypothesizes that weak bounds of water molecules with the CO_3^{2-} anion are quasi-stabilized and structured by the magnetic exposure, so that they inhibit the precipitation rate of CaCO_3 crystals.

We call the second mechanism, which involves the magnetic effect on existing CaCO_3 particles present in water, as *particle mechanism*. Wang [7], using turbidity measurements, observed a faster precipitation of calcium carbonate in the presence of a magnetic field of up to 8000 Gauss under quiescent condition than in non-magnetic treatment.

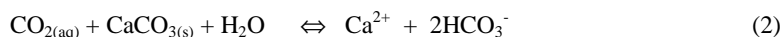
Dynamic fluid system is most commercial magnetic devices for scale control system, where treated water flows through a perpendicular magnetic field. Theoretically, in addition to the ionic and particle mechanism effect in static fluid system, Lorentz forces effect can occur in dynamic fluid. Lorentz force acts on every electrical charged particle, when it is moving through the applied magnetic field. Kozic said that Lorentz force effect on collision probability of dispersed particles causes essential local shifts of ions and particles in electric double layer, which can affect the aggregation and crystallization processes [1]. While in the same time, a conducting fluid flows through the magnetic field, an electric field is generated also according to Faraday's law and produces a potential difference that can cause a current to flow in the fluid according to Ohm's law. The presence of the induced current in the fluid and the applied magnetic field, in turn, produce a mechanical force on the fluid known as a ponderomotive force. This force flattens the profile which can ultimately result in the formation of a boundary layer near the walls. Formation of this boundary layer results in a larger velocity gradient and can trigger CaCO_3 precipitation. This effect is called magneto-hydrodynamic effect [8].

The present study was designed to test and evaluate both static and dynamic fluid systems under magnetic field by examining the amount of CaCO_3 precipitation in solution.

2. EXPERIMENTAL

2.1 Hard Water Preparation

In order to avoid any side effect by foreign ions, carbonized aqueous solutions, (water containing only Ca^{2+} , CO_3^{2-} and HCO_3^- ions) was used. It was prepared by dissolving 0.5 g dm^{-3} reagent grade CaCO_3 in de-ionized water, by bubbling carbon dioxide during 6 hours according to:



The solution was filtered and has produced ± 450 ppm hardness as CaCO_3 . This hardness can be considered as moderate by comparison with the values used by many authors [9], [6], [7], [10]. The pH of solution resulting from this preparation was about 6.4. Then, the carbonized aqueous solutions were displaced towards super saturation by adjusting the pH between 6.4 and 8.5 with was added 1 M NaOH solution.

2.2. Magnetic Water Treatment

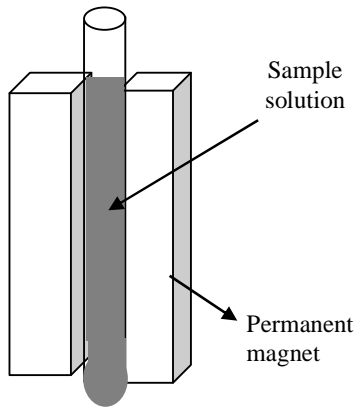
The experiment consists of two parts. The first part of the experiment used the static fluid system. In this method, for each run a magnetic field of a given flux density for a given period of time were exposed to carbonized aqueous solutions magnetization in reaction tube under quiescent condition. Static magnetic field was produced by a pair of neodymium permanent magnets fixed to an aluminum frame with the N/S poles 15 mm apart. An average magnetic flux density (B) of 3400 Gauss was produced, as measured at the center of the two poles with a Hall probe (Hirst GM 04).

The second part of experiment used dynamic fluid system. 400 mL of the sample solution is filled into a glass container, to the outflow of which a silicon tube is attached. The tube leads through a laboratory peristaltic pump (Master flex L/STM), employed to generate fluid flow at variable flow rates (range ca. 0.12 - 22 ml/sec), then through the treatment area of the system, and back to the container, thus forming a closed, recirculation dynamic fluid system. Neodymium permanent magnets employed to generate homogeneous Magnetic field. It consisted of a series of pairs of permanent magnets with north and south poles facing each other, which associated alternately. A Silicon tubing 2 m of total length and 0.7 cm with internal diameter was used. An average magnetic of 5200 Gauss has been produced at the gap between the poles in magnetization area. The temperature of the solution in magnetization process was not controlled, and equal to the ambient temperature of the surroundings (*i.e.*, room temperature, 28 – 29 °C). Fig. 1 shows a simplified schematic of the experimental treatment system used in the presented work.

2.3 Precipitation test

20 ml of the solutions, which were put in precipitation glass reaction tubes (15 mm (OD) x 140 mm (H)) right after the completion of magnetic exposure both in static and dynamic fluid system. The Ca^{2+} concentration in the precipitation tube was analyzed by EDTA complexometry (accuracy $\approx 0.05 \text{ mg as CaCO}_3$), and amount of ions Ca^{2+} consumed in solution as a measure of CaCO_3 precipitation.

Magnetic treatment in static fluid system



Magnetic treatment in dynamic fluid system

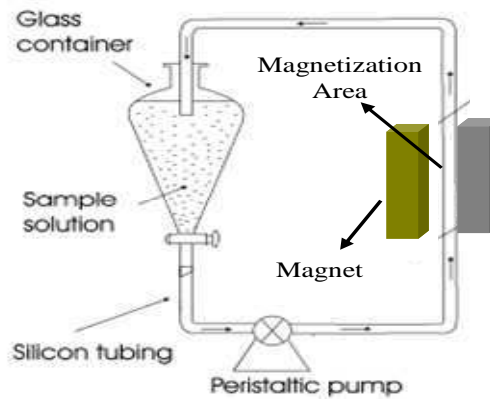


Fig. 1. Schematic of the experimental treatments system

3. RESULTS

The Results will be addressed into the following sections, *i.e.* given in two sections that is magnetization in static fluid system and magnetization in dynamic fluid system. The effects of circulating time, pH, and flow rate on CaCO_3 precipitation process will also be discussed.

3.1 Magnetization in static fluid system

Magnetization and precipitation processes have been conducted in the same tube for 180 minutes at room temperature. Fig. 2 shows the characteristics of CaCO_3 precipitation at varied pH solution under a magnetic field. The CaCO_3 precipitation under magnetic treatment is lowered than that non-magnetic treatment within the range of pH 6.4 – 8. On the other hand the contrary result occurs in pH 8.5.

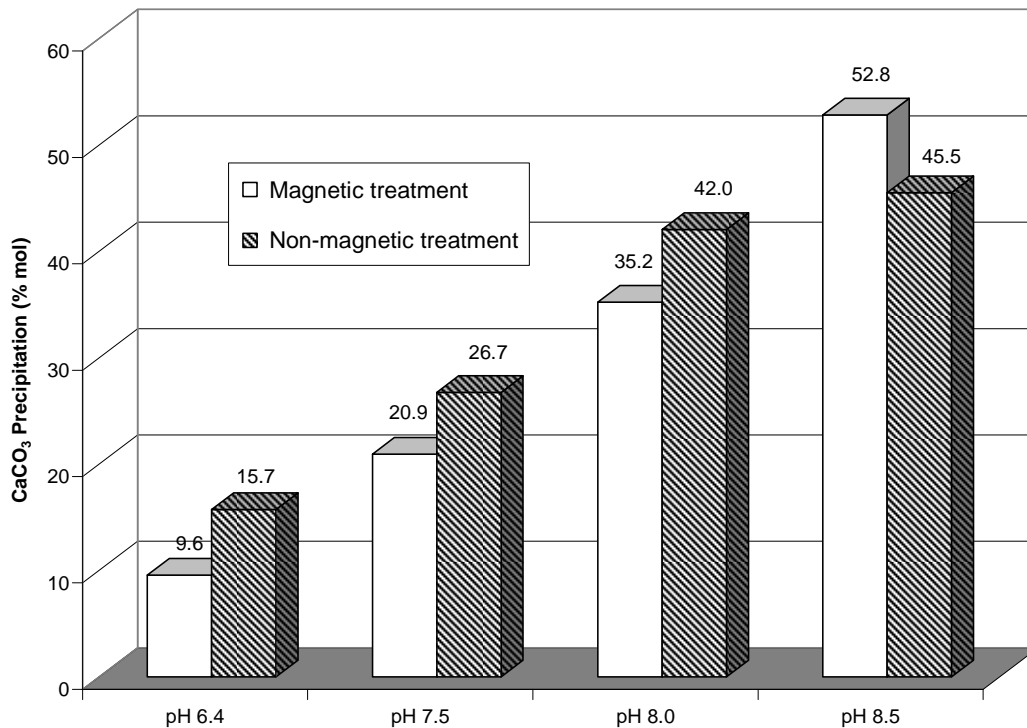


Fig. 2. Percent CaCO₃ precipitation of magnetic and non-magnetic treatments at various pH of solution during 180 minute precipitation and magnetization processes in static fluid system.

It is widely known that the pH of CaCO₃ solution influences the saturation and precipitation of CaCO₃ in the solution. Fathi [11] have found that the saturation level of 500 ppm CaCO₃ solution at pH 7.5 is 15 times than its solubility.

In the CaCO₃ suspension, the CaCO₃ compound might be found as dissolve CaCO₃ (*i.e.* Ca²⁺, CHO₃⁻, CO₃²⁻) as well as CaCO₃ particles in the suspension. Table 1 shows the mol fraction of CaCO₃ as ionic solution and as particles in initial precipitation. Increasing pH of solution will enhance the fraction of CaCO₃ particles. The ionic content in the solution within pH range spans from 6.4 to 8 are 100 to 77.2 % in which ionic mechanism effect is predominant in CaCO₃ precipitation under magnetic field. This effect reduces CaCO₃ precipitation as shown in Fig. 2. The CaCO₃ particle content in the solution of pH 8.5 was 33.8 % in which that the particle mechanism effect is predominant in CaCO₃ precipitation under magnetic field. This effect increases CaCO₃ precipitation as shown in Fig. 2.

Table. 1. Mol percent of CaCO₃ at various pH of solution at initial CaCO₃ precipitation

pH solution	CaCO ₃ as ionic solution (% mol)	CaCO ₃ as particle (% mol)
6.4	100	0
7.5	93.0	6.9
8.0	77.3	22.7
8.5	65.2	33.8

3.2 Magnetization in dynamic fluid system

This section addresses the effects of circulation time, flow rate, and pH of solution in the CaCO₃ precipitation process. Initial Precipitation happened in circulation process (dynamic precipitation) and further the precipitation occurred in precipitation tube (static precipitation). The results of the effect of each variable processes will be presented in the following sections.

3.2.1 Circulation time

Circulation time has a relation to magnetization time in which and the magnetization time will increase by longer of circulation time. Magnetization time (T_m) is duration in which sample is exposed to magnetic field, which is a function of Circulation time (T_c), cross sectional area of pipe (A), volume sample (V), magnet length (l_m). The correlation has been formulated as follows [11]:

$$T_m = \frac{A L_m T_s}{V} \quad (3)$$

Fig. 3 shows that the CaCO₃ precipitation increases with the increased circulation time both in magnetic and non-magnetic treatments. Collision probability of ions or particles increases with increased the circulation time hence raising CaCO₃ precipitation. Magnetic treatment shows that CaCO₃ precipitation is higher than that non-magnetic treatment. The difference of effect of two treatments is the table termed as the increase percentage of CaCO₃ precipitation (See Table 2). The table shows that the increase percentage for 10, 20, 30 minute of circulation time are 100, 79.1, and 66.7 % respectively. This result indicates that magnetic treatment has significant effect especially in initial circulation.

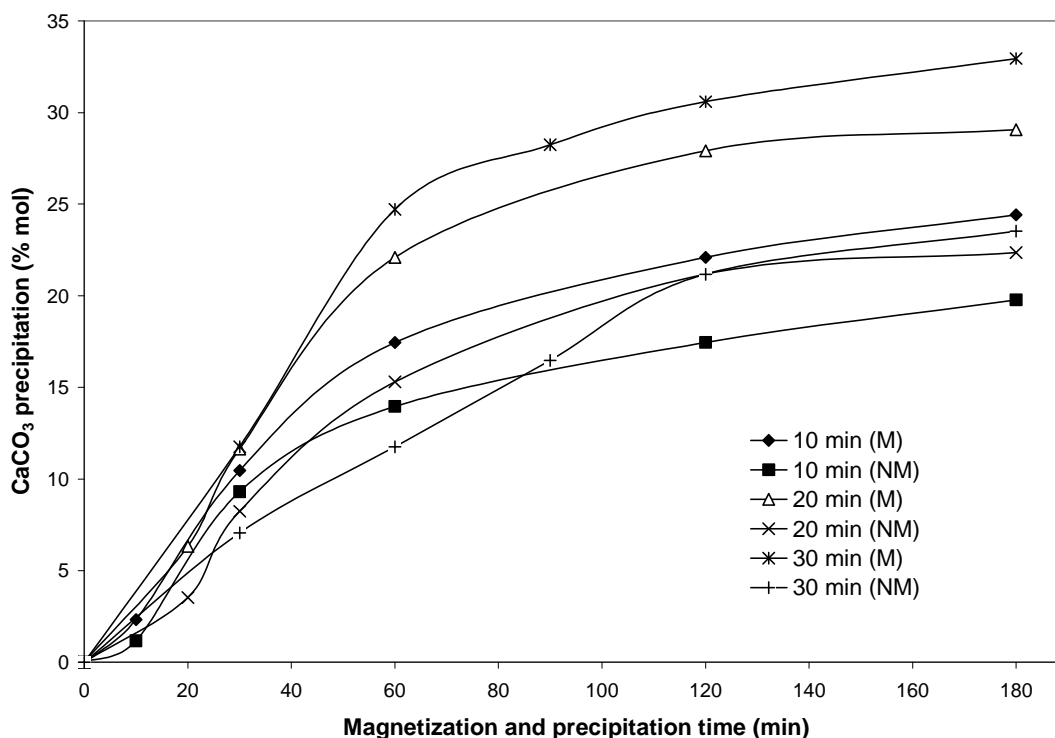


Fig. 3. Percent CaCO_3 precipitation of magnetic treatment (M) and non-magnetic treatment (NM) at various circulation times during 180 minute precipitation process at flow rate 0.93 l/min.

Table 2 Also illustrates that the Increase percentage at 180 minute precipitation for 10, 20, 30 minute of circulation time are 23.5, 30 and 40 % respectively. The precipitation was a combination of circulation precipitation in pipe and static precipitation in tube reaction. Circulation precipitation will lead to nuclei or particles formations, while static precipitation promotes the crystal growth. The result supports the lorentz and magneto-hydrodynamic effect theories that magnetic field increases the ions or particles collisions in CaCO_3 solution in the dynamic fluid system.

Table 2. CaCO_3 precipitation treatments at various circulation times in 180 minute precipitation processes.

	CaCO_3 precipitation (% mol)			
	Circulation time			Precipitation time at 180 min
	10 min	20 min	30 min	
Magnetic treatment (M)	2.3	6.3	11.8	23.5
Non-magnetic treatment (NM)	1.1	3.5	7.1	30.0
Increase percentage $100 \times (M - NM)/NM$	100	79.1	66.7	40.0

3.2.2 Flow rate

Fig. 4 show the effect of flow rate in CaCO_3 precipitation on magnetic and non magnetic treatments. CaCO_3 precipitation increases with increasing flow rate. This is due to the collision probability of ions or particles increases with increased circulation time hence raising CaCO_3 precipitation. Magnetic treatment has always gives effect of higher CaCO_3 precipitation than non-magnetic treatment for all flow rate curves as illustrated in Fig. 4.

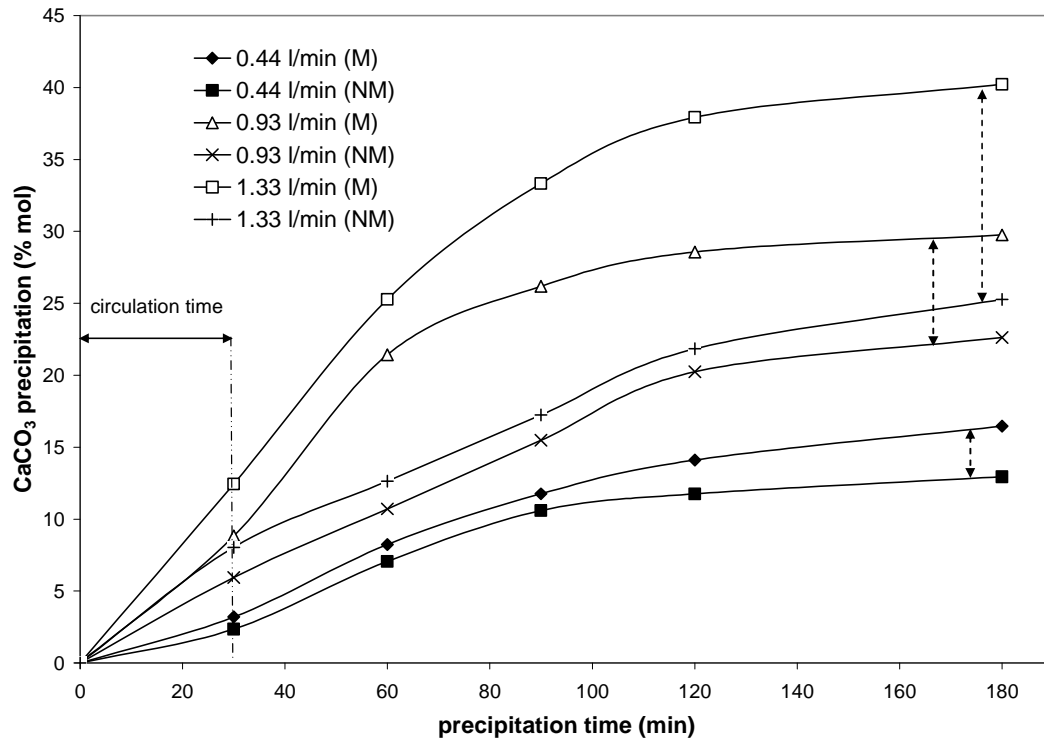


Fig. 4. Percent CaCO₃ precipitation of magnetic treatment (M) and non-magnetic treatment (NM) at various flow rates during 30 minute circulation time and 180 minute precipitation processes.

Table 3 show that increasing flow rate enhances the effect of magnetic treatment which indicates by raising the increase percentage. CaCO₃ precipitation under the magnetic treatment increases up to 59.1 % compared to that non-magnetic treatment at the flow rate 1.33 l/min. The same trend also happens in 180 minute precipitation. The velocity of flow (u) is a function of flow rate (Q) and pipe cross-sectional area (A), which formulated as follows:

$$u = Q / A \quad (4)$$

Table 3. Percent CaCO₃ precipitation at various flow rates during 30 minute circulation time and 180 minute precipitation processes.

	CaCO ₃ precipitation (% mol)					
	Circulating time at 30 min			Precipitation time at 180 min		
	0.44 l/min	0.93 l/min	1.33 l/min	0.44 l/min	0.93 l/min	1.33 l/min
Magnetic treatment (M)	3.2	8.8	12.5	16.5	29.8	40.2
Non-magnetic treatment (NM)	2.4	5.9	8.1	12.9	22.6	25.3
Increase percentage 100 x (M – NM)/NM	33.3	49.2	54.3	27.3	31.6	59.1

Lorentz force (F) which occurs on ions or charged particles when they move through the applied magnetic field is a function of charge (e), velocity of ion or particle (u), and magnetic density (B) as follows:

$$F = e \times u \times B \quad (5)$$

Kozic [1] argues that Lorentz force has significant effect on ion or particle shift in electric double layer (localized shift) which promotes of ions or particles collision reactions.

Magneto-hydrodynamic effect or pendoromotive force appear as a result of the existence of electric current in conducting fluid flow such as CaCO₃ solution through magnetic field. Bush [8] said that the force is proportional to flow velocity and magnetic density. This force flattens the profile of fluid flow which causes high shear force near the wall of the pipe and triggers CaCO₃ precipitation.

Fig. 5 and Table 4 support the Lorentz force effect and magneto-hydrodynamic effect theory on CaCO_3 precipitation under magnetic field in dynamic fluid system.

3.2.3 pH of solution

This section focuses on the role of acidity (pH) on CaCO_3 precipitation under the magnetic field. Fig. 5 illustrates the increase of CaCO_3 precipitation with increased the pH of solution. This occurs due to higher pH which leads to the increase of the saturation of solution hence promoting CaCO_3 precipitation. CaCO_3 precipitation under the magnetic treatment is higher than that non-magnetic treatment on every pH value set in the experiment. We conclude that magnetic treatment has significant effect in pH range of 6.4 to 8.

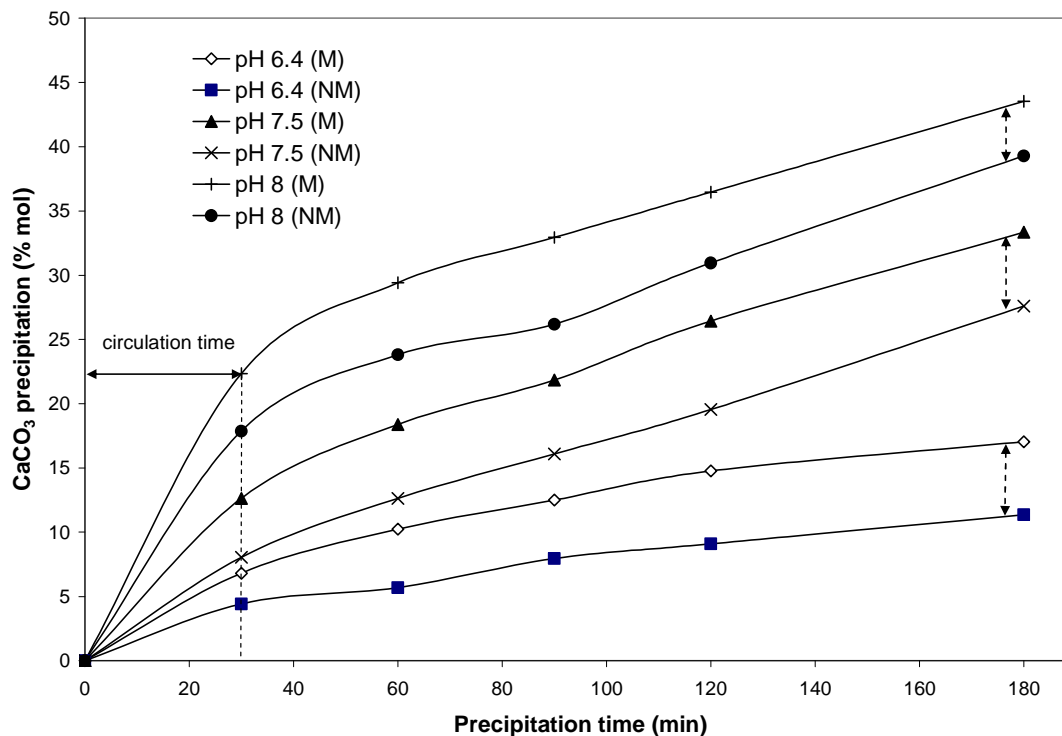


Fig. 5. Percent CaCO_3 precipitation of magnetic treatment (M) and non-magnetic treatment (NM) at various pH of solution during 30 minute circulation time and 180 minute precipitation processes.

Table 4 shows the increase of pH will increase CaCO_3 precipitation. It can be seen on reduction of increase percentage from 54.9 % at pH 6.4 to only 9 % at pH 8. The same trend has also happened in 180 minute precipitation in which 50 % at pH 6.4 reduces to only 10.8 % at pH 8. CaCO_3 solution at high pH (highly saturated solution) will accelerate the formation of particles or nuclei at early precipitation. Furthermore particles formed facilitate the crystal growth and promotes the CaCO_3 precipitation.

The formation of many CaCO_3 particles in early precipitation suggest has significant role on increase the next precipitation. This process consequently reduces the magnetic effect. Lundager [12], [13] has found the similar result and concluded that magnetic field accelerated CaCO_3 precipitation by promoting the transformation of HCO_3^- to CO_3^{2-} and it was followed by CaCO_3 spontaneous formation. HCO_3^- ion species formed in the acid solution (pH 6 - 7).

Table 4. CaCO_3 precipitation at various pH of solution during 30 minute circulation time and 180 minute precipitation processes.

	CaCO_3 precipitation (% mol)					
	Circulation time at 30 min			Precipitation time at 180 min		
	pH 6.4	pH 7.5	pH 8	pH 6.4	pH 7.5	pH 8
Magnetic treatment (M)	4.42	8.05	17.86	11.4	27.6	39.3
Non-magnetic Treatment (NM)	6.82	11.21	19.46	17.0	33.3	43.5

Increase percentage 100 x (M – NM)/NM	54.3	39.3	9.0	50.0	20.8	10.8
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4. CONCLUSION

This research explains the effect of magnetic field on CaCO₃ precipitation, using static and dynamic fluid systems. Magnetization of CaCO₃ solution in static fluid system in pH range of 6.4 – 8 decreases CaCO₃ precipitation and increase CaCO₃ precipitation in pH 8.5 compared to non-magnetic treatment.

CaCO₃ precipitation will increase by increasing circulation time, flow rate, and pH of solution in dynamic fluid system. Magnetization of CaCO₃ solution in dynamic fluid system increases CaCO₃ precipitation.

The magnetic effect on dynamic fluid system is indicated in increase percentage of CaCO₃ precipitation. Increase percentage of CaCO₃ precipitation decreases from 100 % at 10 minute circulation time to 66,7 % at 30 minute circulation time. The increase percentage also increases from 54.3 % to only 9 % when pH of solution increases from 6.4 to 8. Increase percentage of CaCO₃ precipitation increases from 33.3 % at flow rate 0.44 l/min to 54.3 % at flow rate 1.33 l/min.

The results suggest that the effects of magnetic treatment on static and dynamic systems may occur in different phenomena. In Static fluid system, magnetic field strengthens hydrate structure in magnetized ions, which reduce precipitation process. However, in dynamic fluid system, Lorentz force and magneto-hydrodynamic effect on charged ions or particles played important role in increasing CaCO₃ precipitation.

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